

Estimating Water Footprint and Managing Biorefinery Wastewater in the Production of Bio-based Renewable Diesel Blendstock

Energy Systems Division

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by
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NOMENCLATURE AND ABBREVIATIONS

Argonne	Argonne National Laboratory
BETO	Bioenergy Technologies Office
Blue water	Surface water and groundwater used in the production of goods or services
CBOD	Carbonaceous biochemical oxygen demand
COD	Chemical oxygen demand
DOE	U.S. Department of Energy
d.s.t.	dry short ton
ET	Evapotranspiration.
gal	Gallon(s)
Green water	Rainwater stored in soil as soil moisture to support crop growth through evapotranspiration
Grey water	Volume of freshwater that is required to assimilate the load of nutrients/chemicals discharged from production of goods or services based on water quality standards established by regulatory agency
ISO	International Organization for Standardization
kWh	kilowatt-hour(s)
L	liters(s)
lb	pound(s)
mg	milligram(s)
MG	Millions of gallons
MGD	Millions of gallons per day
MM	Million(s)
MXG	<i>Miscanthus × giganteus (Miscanthus)</i> . A large, perennial grass hybrid of <i>Miscanthus sinensis</i> and <i>Miscanthus sacchariflorus</i>
NH ₄ -N	Ammonium
NREL	National Renewable Energy Laboratory
RDB	Renewable diesel blendstock
SWG	Switchgrass, a perennial warm season native bunchgrass; one of the dominant species of central North America

TKN	Total Kjeldahl nitrogen
TS	Total Solids
TSS	Total suspended solids
USDA	U.S. Department of Agriculture
WATER	Water analysis tool for energy resources
WF	Water footprint; water used in the production of goods or services
WWT	Wastewater treatment
WWTP	Wastewater treatment plant
yr	year

EXECUTIVE SUMMARY

This study estimates the water footprint of a renewable diesel blendstock (RDB) produced from cellulosic sugar via a sugar-to-hydrocarbon process and investigates wastewater treatment options. This work, an integral part of the Biofuel Sustainability Program in the U.S. Department of Energy’s (DOE) Bioenergy Technologies Office, is based on a process design report by the National Renewable Energy Laboratory (NREL) (Davis et al. 2013). Davis et al. simulated process water use through an Aspen model, and the design of wastewater treatment (WWT) was contracted to Brown and Caldwell by the NREL (Steinwinder et al. 2011; Gerhardt 2012).

This analysis covers the entire biorefinery operation. The study focuses on net water consumed for the production of a unit of biofuel: blue, green, and grey water footprint. Blue water is defined as the water consumed in the biorefinery that is withdrawn from surface and ground water. Blue water footprint includes enzyme cultivation, pretreatment, hydrolysis, bioreactor, cooling system, boiler, fuel upgrading, combustor track, and on-site WWT. Grey water is defined as wastewater generated from the biorefinery and was evaluated based on the wastewater treatment plant design. Green water, defined as rainwater consumed for the production, is not required in the RDB process.

Figure S1 presents a geospatial distribution of the biorefinery blue water footprint of the corn stover-based sugar-to-hydrocarbon pathway in the contiguous United States.

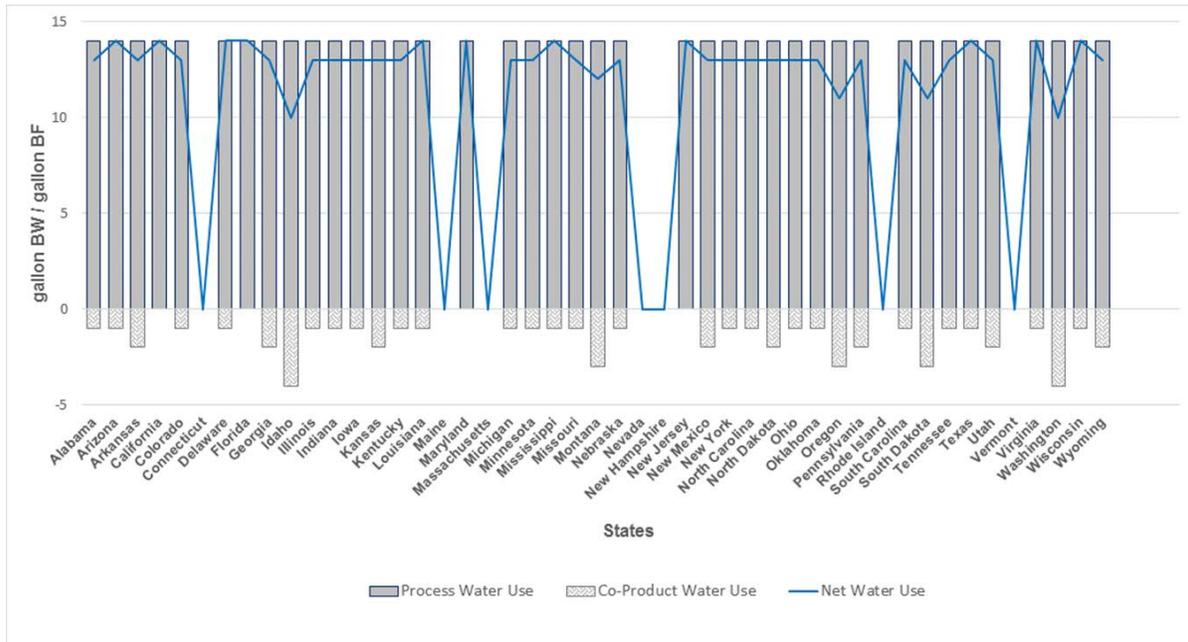


FIGURE S1 Blue water footprints of RDB produced by biorefineries from corn stover via the sugar-to-hydrocarbon process in the contiguous United States. Note: BF = Biofuel

Figure S2 summarizes the grey water footprint of regional perennial grasses-based feedstock for the production of RDB in the 48 contiguous United States under a proposed future scenario (DOE 2011).

Approximately 7–15 gal of water are required to produce a gallon of RDB when corn stover or non-irrigated perennial grasses, switchgrass and *Miscanthus x giganteus* (*Miscanthus*), serve as the feedstock in the contiguous United States. Bioelectricity generation from the biorefinery resulted in a net water credit, which reduced the water footprint. The life cycle grey water footprint for nitrogen is primarily from nitrogen in the feedstock production stage because no wastewater is discharged into the environment in the RDB process. Perennial grasses-based RDB production shows a promising grey water footprint, while corn stover-based RDB production has a relatively low green water footprint.

Results from the study can help improve our understanding of the water sustainability of advanced biofuel technology under development. Make-up water for cooling and boiling remains a major demand in the biorefinery. The work revealed a key issue or trade-off between achieving zero liquid discharge to maximize water resource use and potentially increasing cost of fuel production. Solid waste disposal was identified as a management issue, and its inverse relationship with wastewater management could affect economic sustainability.

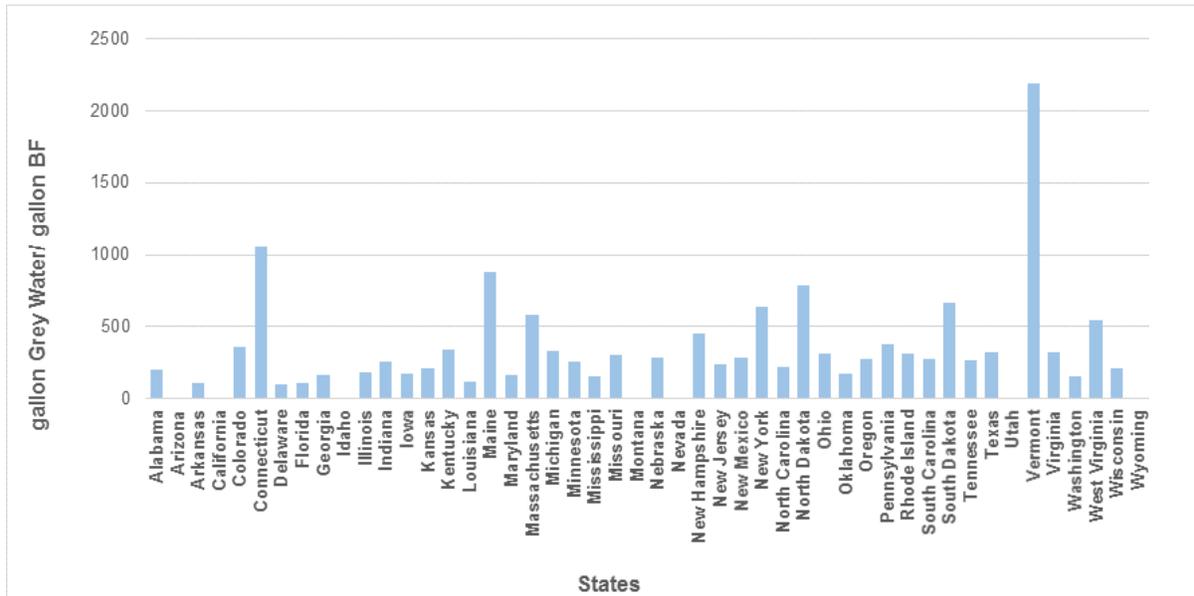


FIGURE S2 Grey water footprint of the RDB produced from perennial grasses via the sugar-to-hydrocarbon pathway in the contiguous United States under a proposed future scenario. Note: BF = Biofuel

ESTIMATING WATER FOOTPRINT AND MANAGING BIOREFINERY WASTEWATER IN THE PRODUCTION OF BIO-BASED RENEWABLE DIESEL BLENDSTOCK

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1 INTRODUCTION

Water use and wastewater release are two key issues associated with water sustainability in biofuel development. An increase in biofuel production would increase the demand for water, and if the increased production was not managed appropriately, the detrimental effects on water quality (health effect due to high nitrate level, threat to aquatic species due to low oxygen level, etc.) could accelerate. Water resources, which vary regionally, are affected by region-specific climate and soil. Water use in biofuel production is feedstock-specific and technology-dependent. Therefore, water resource use is an essential environmental decision criterion in selecting sites for biorefineries and planning cultivation areas for feedstock in biofuel development. Uncertainty regarding a water resource's availability and sufficiency can become a barrier to financing biorefineries, ultimately limiting the deployment of the production of advanced biofuels and bio-based products. In this context, biofuel water use, water resource availability, and the impact of water quality must be evaluated with spatial resolution over the product's life cycle. Quantitative assessment of the environmental sustainability index can support state and local government and industry for informed decision making. This assessment is even more critical when evaluating new technology and processes under development.

Water footprint assessment is widely used as a tool to derive water use metrics—green water, blue water, and grey water footprint—in support of research and development, and decision making. Green water represents rainwater used to support crop growth through evapotranspiration (ET). Blue water represents surface water and groundwater use by crops through ET and in the production of fuels, energy, and other goods. Grey water is an index defined as the volume of freshwater required to assimilate the load of nutrients/chemicals in the wastewater generated from the system, based on water quality standards established by regulatory agency. Chapagain and Hoekstra (2004) proposed a water footprint accounting methodology for products, countries, and regions, which has been incorporated into the International Organization for Standardization (ISO) 14046. The method provides principles, requirements, and guidelines for conducting and reporting a water footprint assessment, either stand-alone or as part of a more comprehensive environmental assessment.

Extensive studies have been conducted in the last decade to examine water use in the production of various biofuels across the major stages of the biofuel supply chain (Berger et al. 2015; Mangmeechai and Pavasant 2013; Wu et al. 2014; Chiu and Wu 2013a; Chiu and Wu 2013b; Wu et al. 2012; Chiu and Wu 2012; Yeh et al. 2011; Scown et al. 2011; Wu et al. 2011, 2009; Gerbens-Leenes et al. 2009; Gerbens-Leenes and Hoekstra 2009; Evans and Cohen 2009; King and Webber 2008). The feedstock analyzed by these researchers includes corn, soybean,

cassava, molasses, sugar crops, agricultural residue, herbaceous grass, and forest wood. Staples et al. (2013) analyzed water and land requirements in irrigated and rain-fed agriculture for the production of jet fuel in the United States. Unger et al. (2013) and Franke and Mathews (2013) expanded grey water footprint analysis in industry production processes from nitrogen to a broader range of chemicals. Berger et al. (2015) compared the trade-offs between carbon and water footprints in European biofuel production.

With the support of the Bioenergy Technologies Office, Argonne National Laboratory (Argonne) developed a water footprint framework and established a national-scale, county-resolution water footprint for biofuels. The biofuel water footprint accounts for both direct water use (consumed through ET, irrigation, and process water) and indirect water use (consumed to produce required inputs) in feedstock and conversion stages of biofuel production. Indirect water use includes water used in petroleum production (conventional, oil sands), electricity generation (e.g., fossil, nuclear, solar, wind, geothermal, hydro), and other inputs. To date, we have developed water footprint assessments for biofuels produced from conventional biofuels (corn, soybeans) (Chiu and Wu 2012), cellulosic biofuels (agriculture residue, perennial grasses, forest wood resources) (Rogers et al. 2016; Muth et al. 2014; Argo et al. 2013; Chiu and Wu 2013a; Wu et al. 2012), and advanced biofuels (algae) (Chiu and Wu 2013b). The water footprint analysis was applied to several biorefinery sizing and logistics system design cases in a multi-laboratory collaboration to evaluate sustainability and profitability. Argonne has assembled a data inventory containing historical climate, land use, agricultural crop, and management information for the contiguous United States at the county level. Building on the data inventory, an on-line model, Water Analysis Tool for Energy Resources (WATER), was developed (Argonne 2015; Wu et al. 2015). WATER contains multiple feedstocks (corn grain; corn stover; wheat straw; switchgrass; *Miscanthus*; short-rotation woody crops willow and poplar; and pine hardwood and softwood), and conversion processes (fast pyrolysis, gasification, hydrolysis and fermentation, and transesterification) for biofuels. It also includes water consumption factors for production of conventional fuels from petroleum, and electricity generation from various fuel sources. Most recently, WATER's grey water analysis further incorporates biorefinery wastewater management and treatment.

The goal of this study is to analyze water use and wastewater management in the production of cellulosic renewable diesel blendstock (RDB) via a sugar-to-hydrocarbon process, currently under development, and its potential regional impact both in water consumption and water quality. The analysis integrates the production process-based water footprint with geospatial water analysis to assess the regional impacts for the contiguous United States with county, state, and region resolution. We conducted a geospatial analysis of water footprint of the RDB produced from several types of cellulosic feedstock under projected future scenarios. A supporting objective of the study is to evaluate wastewater management for the biorefinery from a technology, management, and economic perspective. Results from this study contribute to understanding the potential implications of the newly developed technology and can further inform decision making for research and development, the biofuel industry, feedstock producers, and local and state governments.

2 SCOPE OF THE STUDY

Water footprint—blue, green, and grey—measures the amount of water used for the production of a unit of biofuel through the feedstock and conversion processes. This work evaluates the water footprint of a biorefinery equipped with a cellulosic sugar-to-hydrocarbon conversion process (Davis et al. 2013). Figure 1 illustrates a simplified diagram of the major water flows for the process.

The water footprint analysis covers the major water use stages in the biofuel production life cycle—feedstock production and conversion. Impact of the implementation of the process is assessed for the contiguous United States. This study analyzes water consumption (not water withdrawal), which is the amount of water that leaves the production system in the region and is no longer available for the same region. Corn stover and perennial grass (switchgrass [SWG] and *Miscanthus* [MXG]) are considered cellulosic feedstocks to the conversion process, and are grown in various regions in the United States based on historical conditions or future projections. Blue water footprint includes irrigation water and water used in enzyme cultivation, pretreatment, hydrolysis, bioreactor, cooling system, boiler, fuel upgrading, combustor track, and on-site wastewater treatment (WWT). A grey water footprint is concerned with nitrogen because of the extensive input of fertilizer in the feedstock production stage. Green water use is limited to feedstock, as it is not used in the biorefinery.

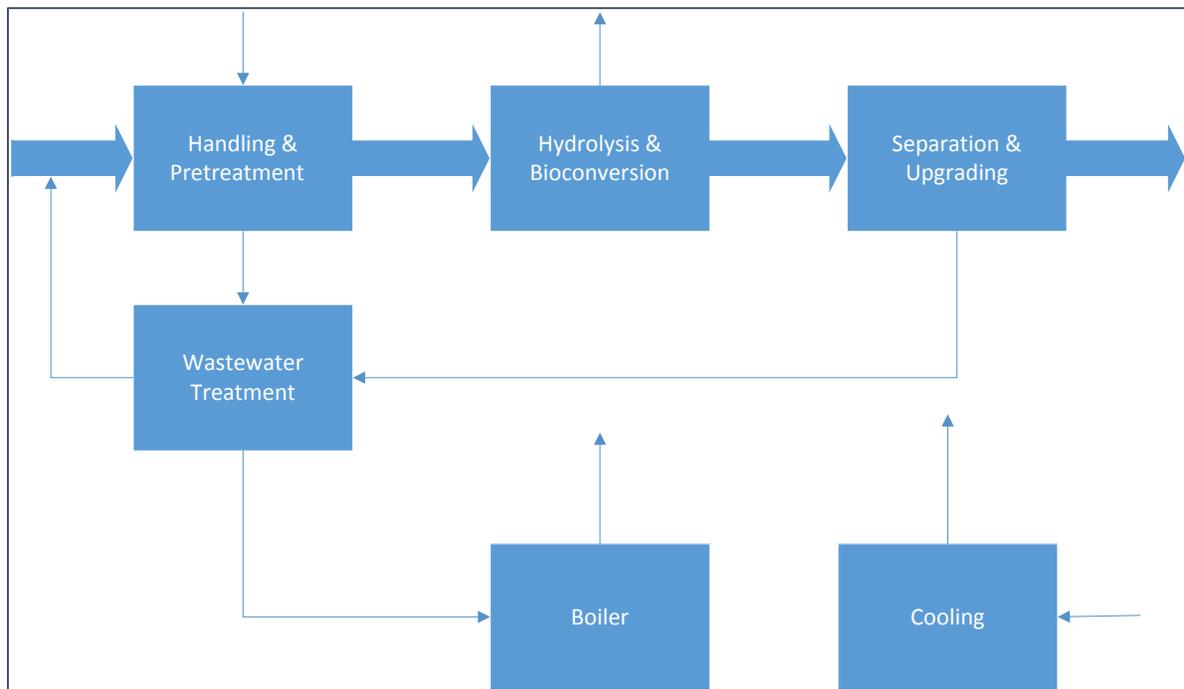


FIGURE 1 Simplified schematic of the sugar-to-hydrocarbon process analyzed in this study. **Note:** Bold arrows represent process flow from feedstock to RDB product; fine lines and arrows illustrate major water flow.

This study reviews wastewater treatment design for the biorefinery, included an exploration of options to use commercially available wastewater treatment processes and facilities for the biorefinery wastewater in an economically competitive manner.

3 METHOD, ASSUMPTIONS, AND DATA SOURCES

In this study, water footprint is analyzed using the WATER model (Argonne 2015) for process specific simulation. The concept and methodology of water footprint accounting was documented elsewhere (Wu et al. 2012; Chiu and Wu 2012). Corn acreage and production are based on historical U.S. Department of Agriculture (USDA) National Agricultural Statistics Service data. Chiu and Wu (2012) document the simulation of corn stover harvest. The SWG and MXG water footprint simulation is reported in Wu and Chiu (2014). A process design report by Davis et al. (2013) has documented mass, energy, and sustainability metrics for the sugar-to-hydrocarbon process simulated through an Aspen model. Assumptions used in the conversion of cellulosic feedstock to sugar are documented in Humbird et al. (2011). A proposed potential future feedstock production scenario for SWG and MXG at 2022, under the farm gate price of \$80 per dry ton with assumed USDA baseline yield, can be found in the open literature (DOE 2011). Major operational parameters for the process are presented in Table 1. The water footprint of the stover is determined using both mass-based and purpose-based allocation. Mass-based allocation assigns estimated water volume to grain or stover based on the mass proportion of the feedstock. Purpose-based allocation assigns irrigation water consumption (blue water) to grain under the assumption that grain production is the primary purpose for growing the corn plant.

The WWT process for this study was based on the conversion process modeling incorporating several sources. The primary source and basis of analysis is the National Renewable Energy Laboratory (NREL) process design report presenting the sugar-to-RDB biorefinery (Davis et al. 2013). The biorefinery's WWT design is based on the results of the NREL commission to Brown and Caldwell by Steinwinder (Steinwinder et al. 2011) and Gerhardt (Gerhardt 2012). In addition, fundamental to the sugar-to-RDB refinery is the work of Humbird et al. (2011). The RDB process adopted Humbird's biological process producing biofuel from stover and switchgrass. These documents serve as the basis for the WWT and management evaluation in this study.

TABLE 1 Major Process Parameters of the Cellulosic Sugar-to-RDB Biorefinery

Product	Process Parameter	Quantity
RDB	Production	31.3 MG /year
	Feedstock	722,864 d.s.t./year
	Yield	43.3 gal/d.s.t.
Electricity	Plant electricity use	11.0 kWh/gal
	Excess electricity for export	2.6 kWh/gal

Note: d.s.t. = dry short ton; kWh = kilowatt-hour(s).

4 RESULTS AND DISCUSSION

4.1 BLUE WATER FOOTPRINT IN THE BIOREFINERY

The biorefinery process includes a blue water and grey water footprint. Water is consumed or lost in multiple steps of the sugar-to-RDB process, including through cooling, aeration, bioreactor vent, pretreatment, enzymatic hydrolysis, boiler blowdown vent, upgrading flue gas, upgrading produced water, WWT evaporation, combustor stack, and WWT brine. As shown in the process water input and output scheme in Table 2, the major water user step in the RDB process is cooling through evaporation and drifting. The cooling operation loses 12 gal of water for every gallon of RDB produced, accounting for 65% of the total process water consumed (18.9 gal). The combustor stack ranks second, consuming 25% of the process water. The two operations combined account for 90% of process water consumed. Water evaporation loss from the bioreactor (bioreactor vent) is a distant third at 4.5%. Almost all of the process water loss is evaporative.

TABLE 2 Water consumption in a biorefinery producing RDB via the sugar-to-hydrocarbon process based on process design

Water Consumption (gallon/gallon RDB)		Water Input and Generation (gallon/gallon RDB)	
Cooling	12.23	Feedstock moisture	1.38
Aeration	0.03	Glucose syrup water content	0.01
Bioreactor vent	0.87	Water in raw chemicals	0.10
Pretreatment	0.16	Water generated in process (combustor, conversion)	2.37
Enzymatic hydrolysis	0.18	Water from air intake (combustor, enzyme, WWT)	0.63
Boiler blowdown vent	0.17		
Upgrading flue gas	0.01		
Upgrading produced water	0.06		
WWT evaporation	0.19		
WWT brine	0.25		
Combustor stack	4.81		
Total	18.90	Total	4.49
Net water consumption (makeup water) (gal/gal RDB)		14.41	
Wastewater treatment and reuse		100%	
Wastewater discharge (gal/gal RDB)		0	

Source: Davis et al. (2013).

Water is consumed in some steps in the biorefinery, but is also accumulated in other steps. A total of 4.49 gal of water enter the biorefinery for every gallon of RDB produced. As shown in Table 2, water is brought to the process by material input (feedstock, glucose syrup, and chemicals) and air intake. A water balance for the biorefinery (Davis et al. 2013) shows that the majority of water input is from water generated in the process through conversion, combustion, and enzyme production (2.37 gal/gallon RDB). This water generation offsets approximately 15% of the total water use (18.9 gal/gallon RDB). Accounting for all inputs and outputs, a net 14.41 gal of water are consumed to produce a gallon of RDB. The water intensity of the sugar-to-RDB process appears considerably higher compared to the 5.4 gal/gallon used in the biochemical fermentation process to produce ethanol. The RDB's high water use intensity is caused partly by its low fuel yield – 43.3 gal RDB per dry short ton (d.s.t.) of feedstock, which is about 60% of the fermentation-based cellulosic ethanol production fuel yield of 70 gal/ d.s.t. In addition, the RDB design increased process steam requirements (Davis et al. 2013).

Nevertheless, the process can generate an excess amount of bioelectricity from lignin combustion (Table 1). This electricity can be used in the biorefinery to replace electricity that would otherwise be purchased from the grid. According to the design, the electricity produced exceeds the on-site power demand for the biorefinery, and can be exported to the grid. It is estimated that 2.6 kWh of excess electricity can be exported for a gallon of biofuel produced. Therefore, the water that would be consumed to generate the electricity supplied to the grid could be avoided, and would become a water consumption credit to attribute to the biorefinery blue water footprint.

Using the process water consumption of 14.41 gal/gallon RDB plus the water credit, the blue water footprint was calculated for the contiguous United States (Figure 2). Because water footprint differs with the fuel source and the technology used to generate electricity, the water credit for the same amount of replacement electricity varies depending on the electricity profile of the state. Results clearly show that, for some states, the water credit from co-product bioelectricity generation can reduce a sizable portion of the water footprint.

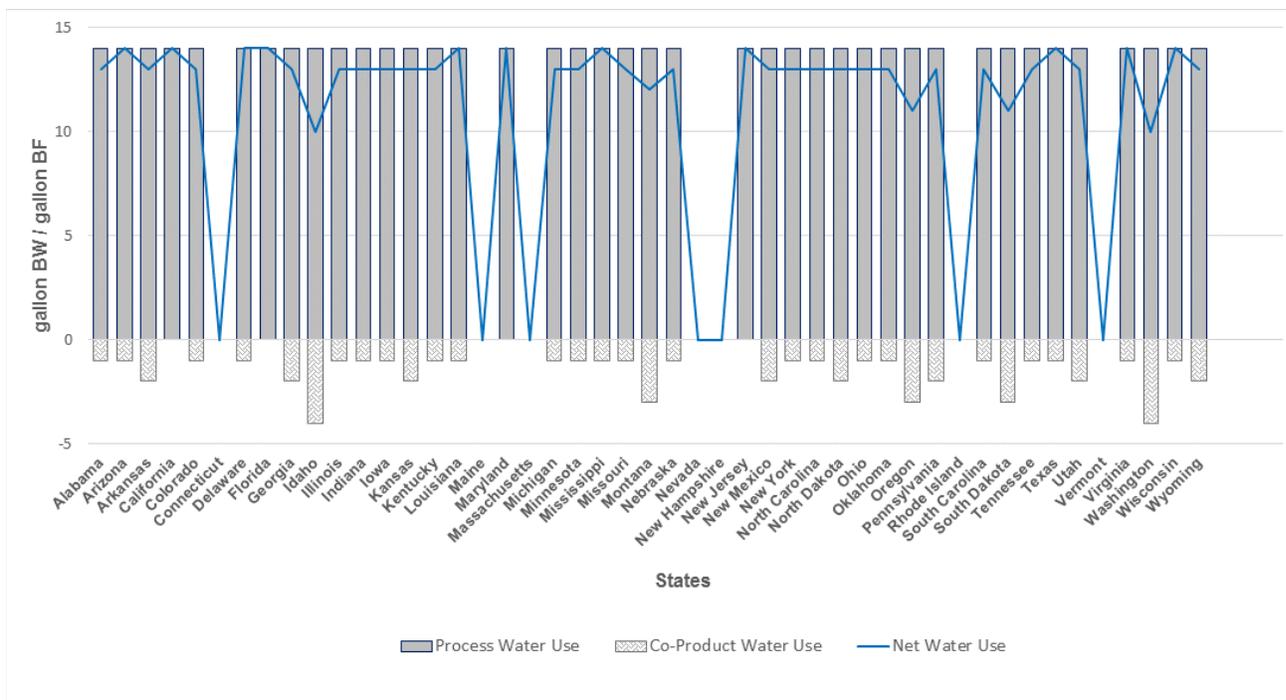


FIGURE 2 Blue water footprints of RDB produced by biorefineries from corn stover via the sugar-to-hydrocarbon process for the contiguous United States.

4.2 BLUE WATER FOOTPRINT OF RENEWABLE DIESEL BLENDSTOCK PRODUCED FROM CELLULOSIC FEEDSTOCK

From a life cycle perspective, major stages of water consumption include feedstock growth and processing. In the feedstock growing stage, consumptive use of irrigation water by the crops constitutes blue water. This study estimated two cellulosic feedstocks: corn stover and perennial grasses switchgrass and *Miscanthus*. The U.S. Department of Energy (DOE) has endorsed that only the perennial grasses growing in regions that do not require irrigation will be considered as potential cellulosic feedstocks for bioenergy production. Therefore, there will be no blue water associated with the perennial grasses in the production scenarios in this study.

Figure 3 illustrates county-level feedstock blue water footprint in the United States when corn stover is used as an RDB feedstock. The corn stover growth and harvest acreages are simulated based on historical land use, also available from WATER (Argonne 2015). The blue water footprint reflects water consumed by irrigation of the growing corn crop, the stover of which is harvested for RDB production. Allocation of water footprint between corn grain and stover is discussed in Section 4.5 of this report.

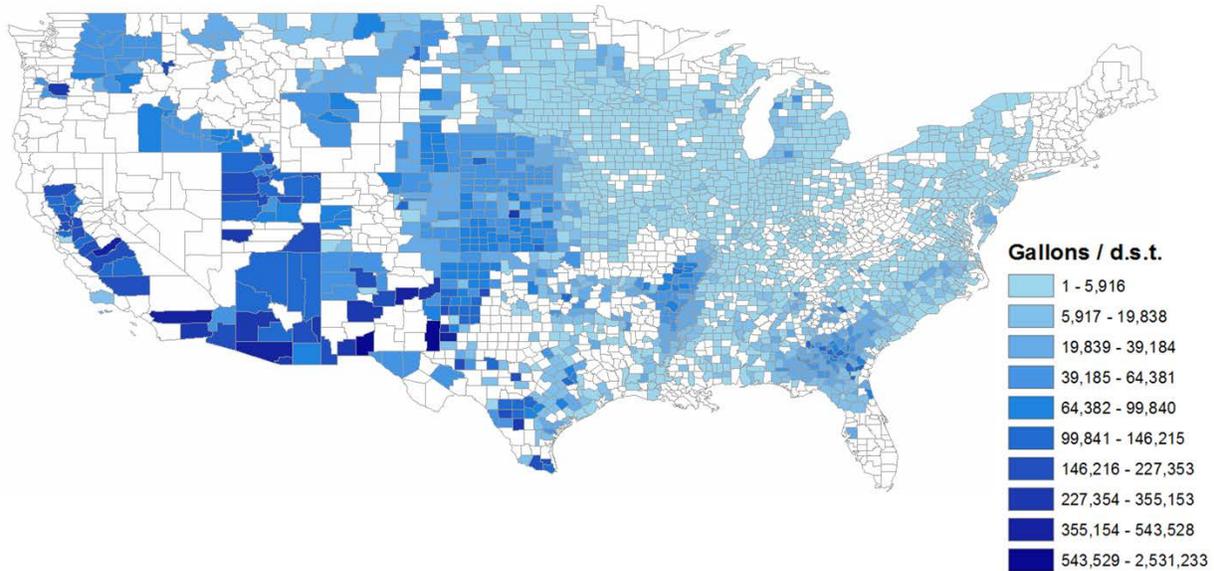


FIGURE 3 County-level blue water intensity distributions for production of RDB from corn stover under a proposed future scenario. Values represent the mass-based water allocation method.

The combined blue water consumption of the agricultural process (growing corn stover for feedstock) and the biorefinery process is presented in Figure 4, a state-level blue water footprint for RDB production for the contiguous United States. Illinois, Iowa, Indiana, Minnesota, Wisconsin, Virginia, and Tennessee have relatively low blue water footprints for the cellulosic RDB while most states in western regions have a high footprint. Finally, the volume of blue water is also dependent on the volume of feedstock produced for bioenergy. Blue water required for growing the feedstock could vary from 15 gal (New York) to 251,000 gal (Nebraska), largely because of significant differences in the feedstock production scale.

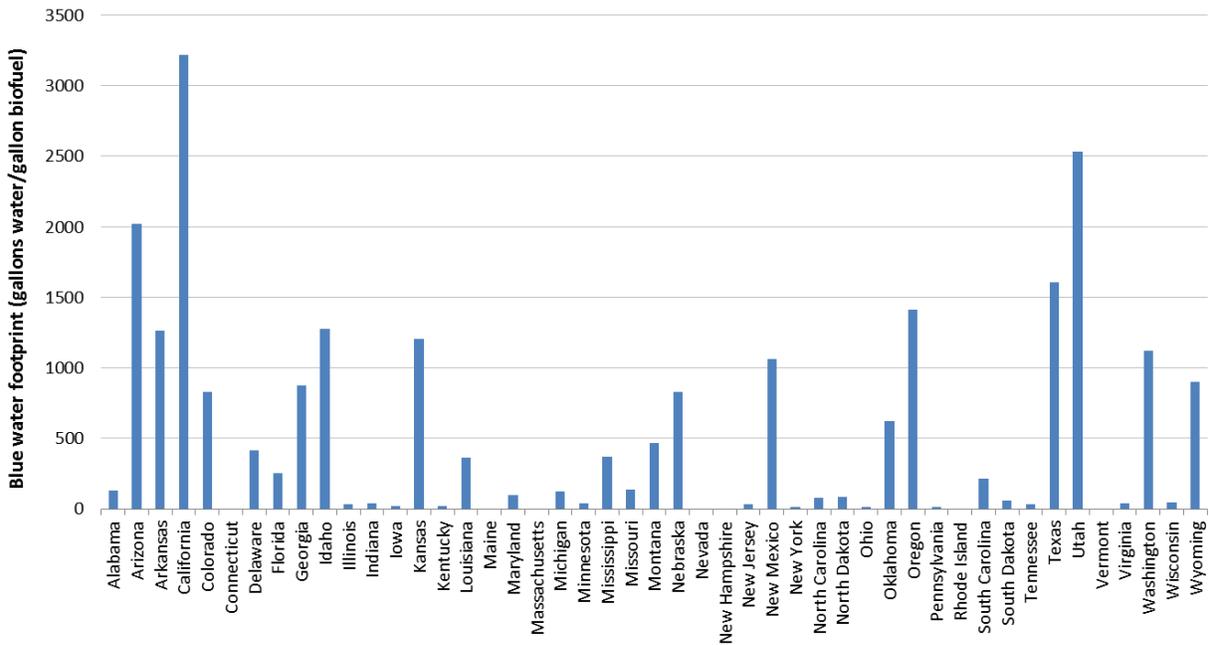


FIGURE 4 Life cycle blue water footprint for production of RDB from corn stover at state and regional levels under a proposed future scenario. Values represent the mass-based water allocation method.

4.3 GREEN WATER FOOTPRINT OF RENEWABLE DIESEL BLENDSTOCK PRODUCED FROM CELLULOSIC FEEDSTOCK

Cellulosic feedstock green water footprint is calculated for corn stover and perennial grasses at county-level based on rainfall, cultivation acreage, and crop production. Corn stover cultivation acreages are based on historical data, while perennial grass acreages are from a proposed future scenario by DOE (2011). The biorefinery process does not consume green water. As shown in Figure 5a, the geographic distribution and intensity of the green water footprint for corn stover appears to complement that of the blue water footprint, because areas that do not receive adequate rainfall require irrigation (blue water) to meet crop water demand. Figures 5a and 5b show that the two feedstocks exhibit a distinct pattern of the green water footprint. Water footprint depends highly on the type of crop, soil condition, regional climate, and crop location as proposed in the scenario (DOE 2011). In the future scenario, western states were not considered appropriate for growing perennial grasses for bioenergy feedstocks, because such cultivation would require irrigation, straining freshwater resources in the water-limited regions.

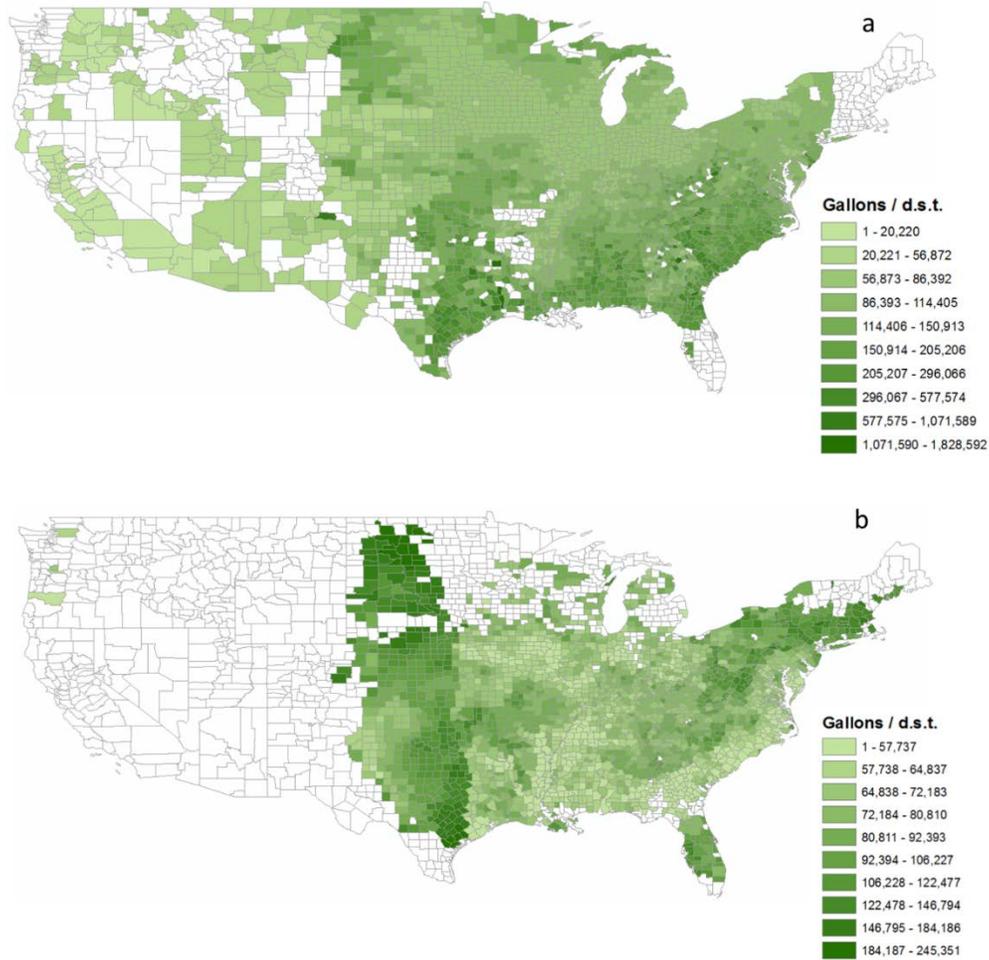


FIGURE 5 County-level green water intensity distributions for production of RDB from cellulosic feedstocks (a) corn stover and (b) switchgrass and *Miscanthus*, under a proposed future scenario. Values for corn stover represent the mass-based allocation method.

The county-level green water footprint is aggregated and weighted to a state average for both corn stover and the perennial grasses. As Figure 6 shows, the green water intensity for perennial grasses tends to be concentrated in the range of 1,000–2,000 gal/gallon of biofuel while corn stover has larger variations from state to state. Although both green and blue water are appropriated in the production of biomass, green water is generally preferred because of its low cost, both economically and environmentally, especially in water-rich regions.

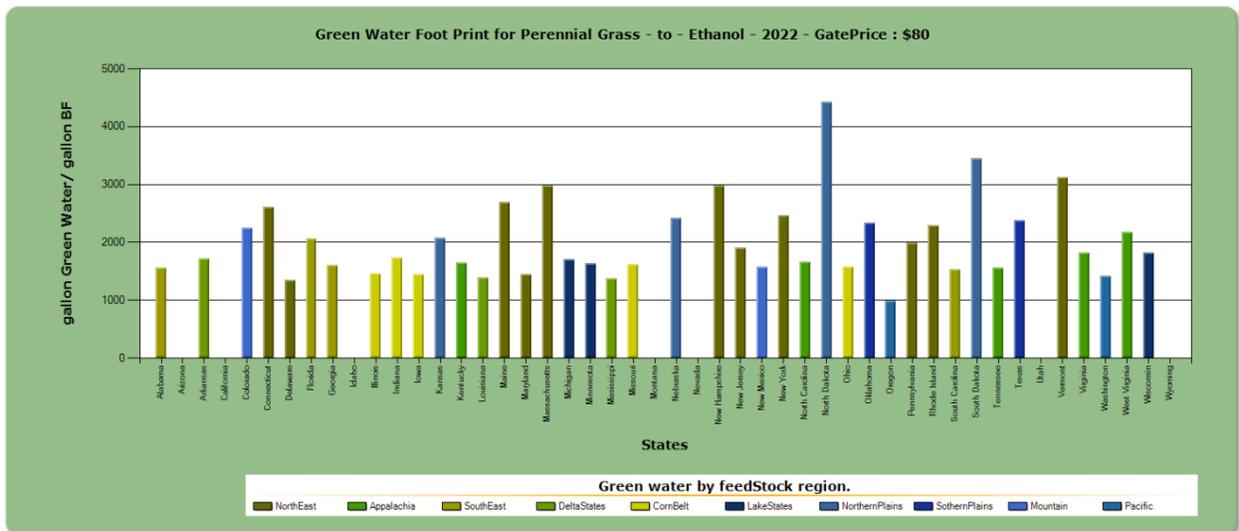
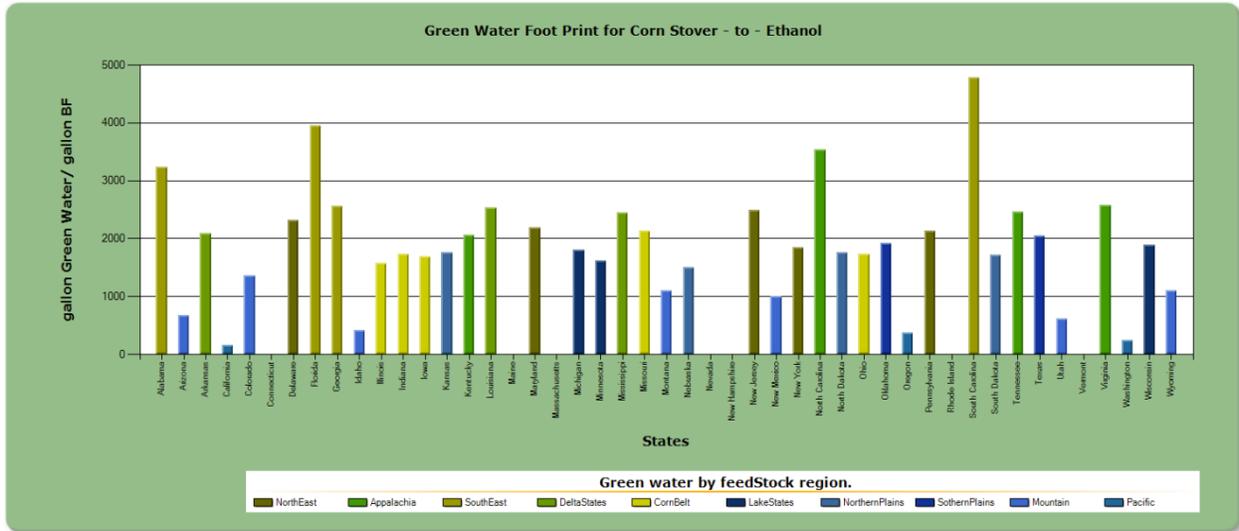


FIGURE 6 State and regional-level green water footprints for production of RDB from (a) corn stover and (b) perennial grasses via the sugar-to-hydrocarbon process under a proposed future scenario. Values represent the mass-based water allocation method.

4.4 GREY WATER FOOTPRINT OF RENEWABLE DIESEL BLENDSTOCK PRODUCED FROM CELLULOSIC FEEDSTOCK

The sugar-to-RDB biorefinery was designed with a multi-stage process waste stream treatment, including recycling and reusing to achieve zero liquid discharge. Thus, the nitrogen grey water analyzed in this study includes fertilizer runoff from the agricultural fields used to cultivate feedstock. Fertilizer input to corn is well documented in USDA data. In comparison, similar data for large-scale perennial grass farms are limited. However, available research already shows that perennial grasses are capable of trapping more nutrients from deep soil using their long roots and require less nitrogen from chemical fertilizer input. Estimates show that the nitrogen fertilizer required by perennial grasses could be half that of corn, resulting in

considerably lower grey water footprints at both county (Figure 7) and state levels (Figure 8). Further, average grey water footprints by state for corn stover vary significantly from a few hundred to more than 4,000 gal/gallon RDB, and in more than half the states exceeds 2,000 gal/gallon RDB. In contrast, for a majority of states, average values of grey water footprints for perennial grasses are less than 500 gal/gallon RDB.

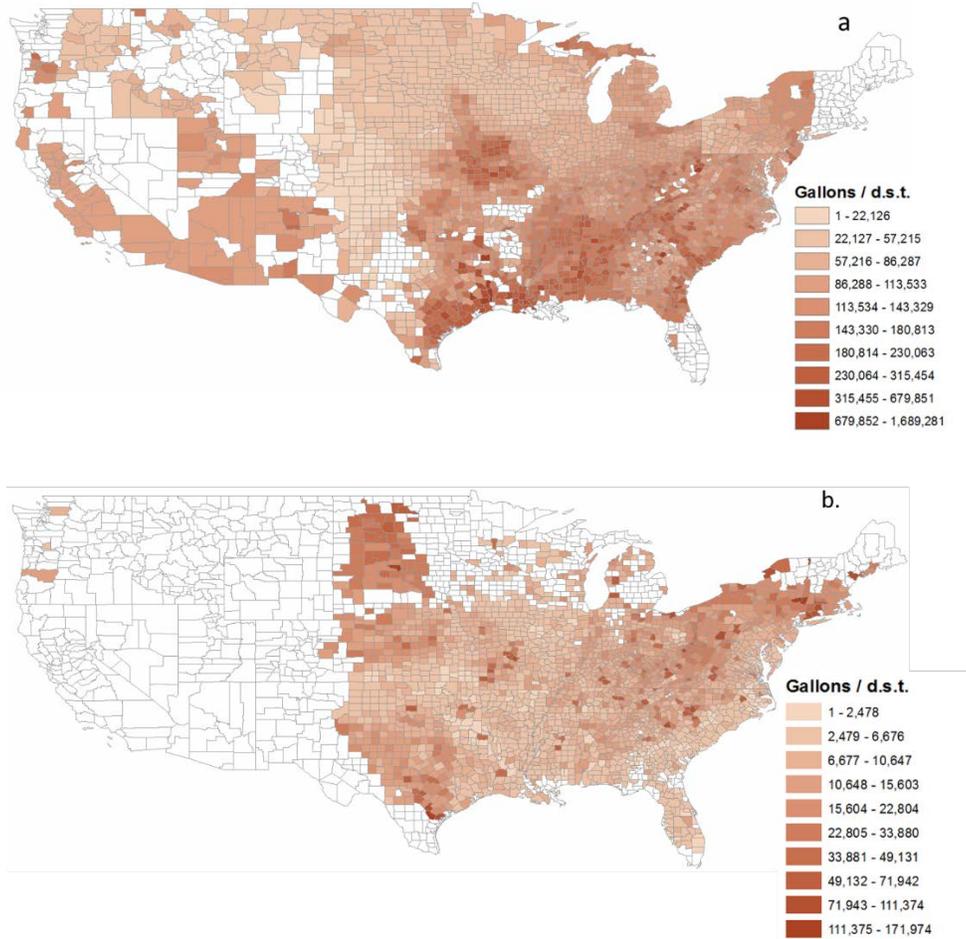


FIGURE 7 County-level grey water intensity distributions for production of RDB from cellulosic feedstocks (a) corn stover and (b) switchgrass and *Miscanthus* under a proposed future scenario.

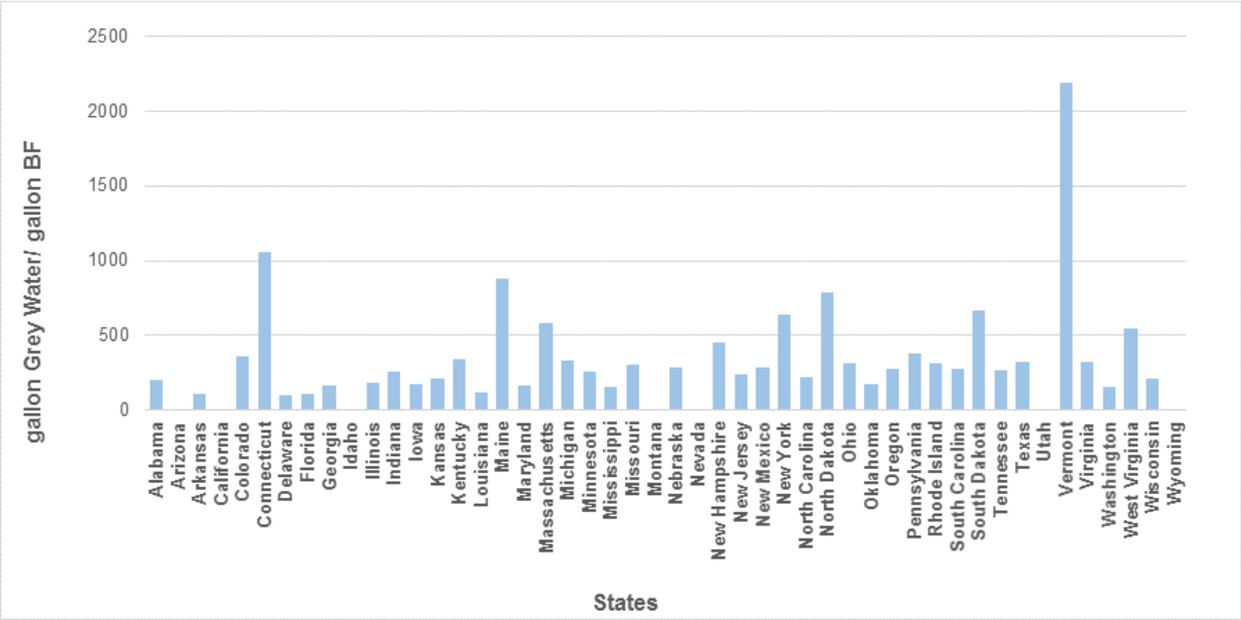
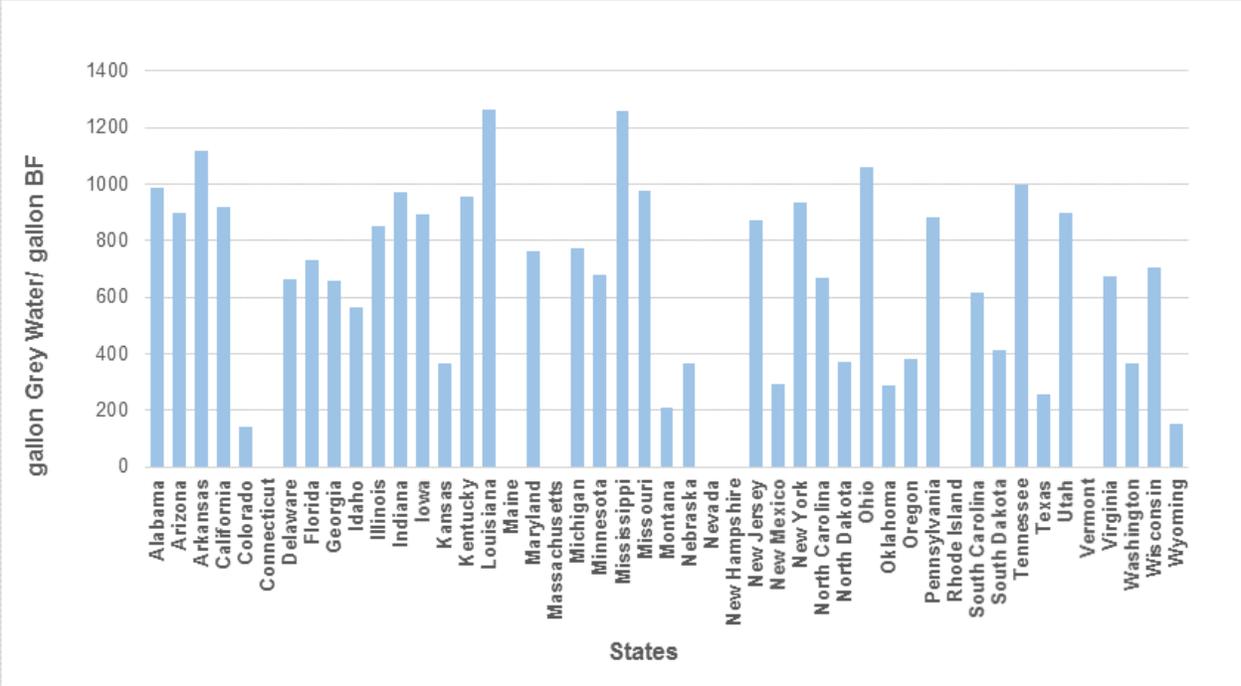


FIGURE 8 State and regional-level grey water footprints for production of RDB from corn stover (upper) and perennial grasses (lower) via the sugar-to-hydrocarbon process under a proposed future scenario. Values represent the mass-based water allocation method.

4.5 EFFECT OF WATER ALLOCATION ON BLUE AND GREY WATER FOOTPRINTS

When a crop produces multiple feedstocks, the water footprint needs to be allocated to the individual feedstocks. In this study, corn crops yield two feedstocks: corn grain and corn stover. Corn stover feeds the sugar-to-RDB biorefinery, and the water footprint associated with growing and harvesting corn stover is accounted for in the RDB water footprint; water consumption associated with growing corn grain is excluded.

Several allocation methods have been developed, including mass-based allocation and purpose-based allocation. The mass-based method allocates water footprints to the feedstocks by mass proportion of the feedstock. Therefore, the corn crop water footprint is partitioned into stover and grain based on the ratio of mass weight of stover and grain.

The purpose-based method allocates water footprint by its cultivation purpose—the determining factor is its purpose for human operational activities. Water footprints from irrigation and fertilizer inputs (blue and grey water) are allocated to the feedstock that is purposely grown.

For example, in current agriculture, corn is primarily grown for the purpose of harvesting grain to support production of animal feed, biofuels, high fructose corn syrup, and other products. Corn stover has been considered an agricultural waste and was typically left behind in the field. Thus, because stover is not purposely grown, it does not share the burden of water footprints resulting from irrigation (blue water). Note that the green water footprint resulting from rainfall is not a part of cultivation operations and, therefore, does not apply.

When stover is collected from the field, the nutrients contained in the stover (nitrogen, phosphorus) that would otherwise release to the soil profile are no longer available. Therefore, supplemental fertilizer is applied to maintain the soil nutrient balance. Grey water resulting from the supplemental fertilizer is accounted for in the purpose-based method.

Both mass-based and purpose-based methods are adopted to address different viewpoints, such as emphasizing physical properties or value. However, results of the study using the two methods are very different. Under the purpose-based method, the blue water footprint in the feedstock stage would be zero for stover. Nitrogen-generated grey water for stover using the purpose-based method (Figures 9 and 10) is only a fraction of that using the mass-based method (Figure 7a) because the amount of supplemental nitrogen fertilizer for corn stover is very small. With this approach, the life cycle blue and grey water footprints of RDB produced from stover would be low.

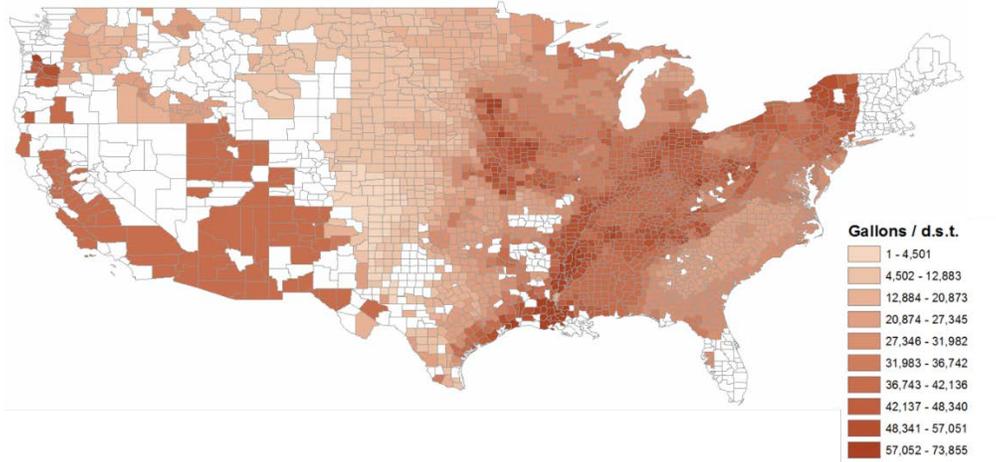


FIGURE 9 County-level grey water footprints for the production of RDB from corn stover. Values represent the purpose-based water allocation method.

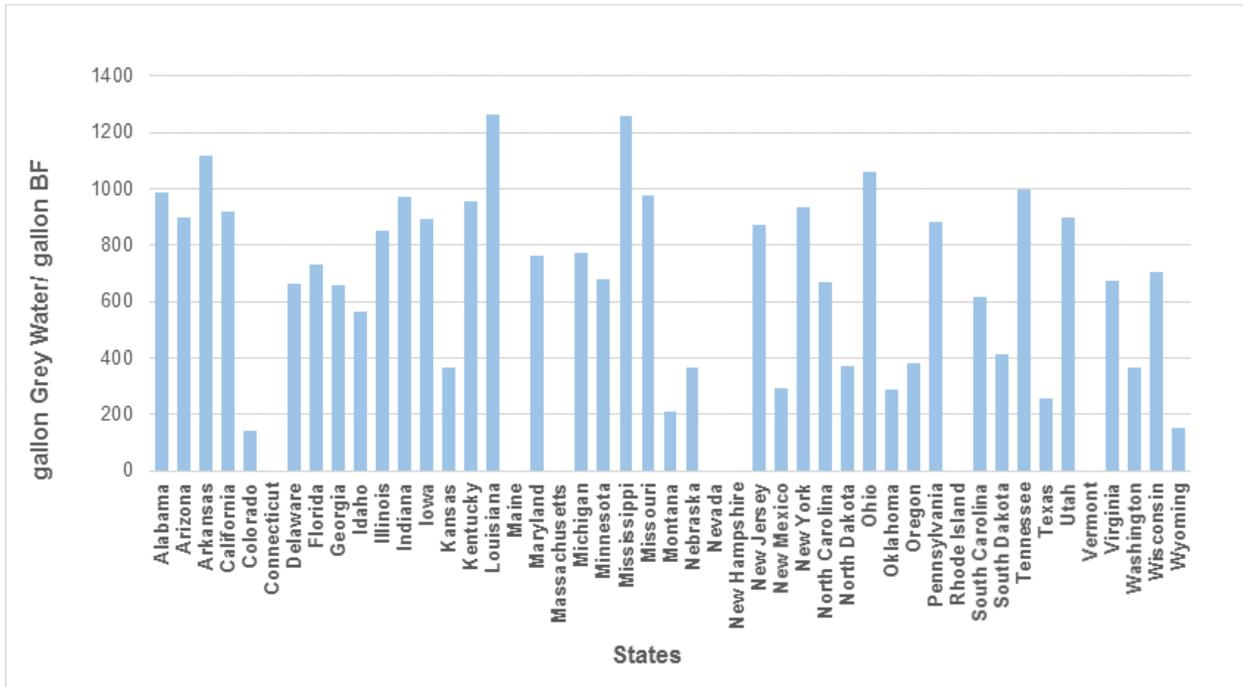


FIGURE 10 State and regional-level grey water footprints for production of RDB from corn stover via the sugar-to-hydrocarbon process under a proposed future scenario. Values represent the purpose-based water allocation method.

4.6 WASTEWATER TREATMENT ANALYSIS

In this section, we reviewed grey water management in the sugar-to-RDB biorefinery with the corn stover feedstock, based on the WWT process designed by Brown and Caldwell and described by Steinwinder et al. (2011) and Gerhardt (2012). One goal of the analysis is to update WWT cost with recent knowledge and development in this field.

4.6.1 Biorefinery Wastewater Treatment Plant Scheme

The process scheme for the wastewater treatment plant (WWTP) is as follows:

The total wastewater stream is sent to an anaerobic treatment reactor, followed by an activated sludge reactor, a membrane filtration process, and finally a reverse osmosis process. The treated liquid is then recycled back to the ethanol plant for use as process water. Biogas is produced in the anaerobic reactor and burned for steam generation. The biological sludge produced in the anaerobic reactors and activated sludge system is dewatered and sent to a biomass burner system. The brine from the reverse osmosis system is also sent to this burner system. It is assumed that the ash from the burner system would be sent to a landfill, but this is not explicitly stated.

An assumption was made that the ethanol plant would be located in a rural area, thereby establishing goals of zero discharge of wastewater and reuse of as much treated wastewater as possible in the ethanol production process. Quantities of biological sludge and brine solution were also to be minimized. Potential alternative technologies were explored (see Appendix).

4.6.2 Assumptions for Wastewater Treatment Influent

A traditional basis for determining an appropriate treatment process for a given industrial wastewater is to assess the type of industry generating the wastewater, the wastewater flow rate, the chemical characteristics of the wastewater, wastewater mass loading rates for key constituents, and the desired final effluent quality from the treatment process.

The 2012 report (Gerhardt 2012) used data from two samples. One wastewater sample, a blend of stillage and black liquor, was collected from the new process in April 2012. Another sample of just the black liquor was collected from a laboratory-scale reactor, also in April 2012. Both samples were analyzed for a variety of chemical constituents, and an “engineering judgement” was made as to how to combine the data to yield a final result for use in the wastewater treatment plant design. The wastewater flow rate was determined by an Aspen model.

It should be noted that there are significant differences in the water quality of the influent to the WWTP between the biorefinery design report (Davis et al. 2013) and the WWTP design reports (Steinwinder 2011; Gerhardt 2012). Table 3 compares the influent wastewater characteristics from Gerhardt (2012) and Davis et al. (2013).

TABLE 3 Comparison of Wastewater Characteristics

Parameter	2012 Report Design Value ^a	2013 Report Design Value ^b
Type of Industry	Agricultural Waste to Biofuel	Agricultural Waste to Biofuel
Influent Flow, MGD	2.7	1.6
Influent Temperature, °C	30–50	35–57
Influent Total COD, mg/L	66,600	120,000
Total COD Loading, lb/day	1,499,698	1,601,280
Influent TS, mg/L	39,900	130,000
TS Loading, lb/day	898,468	1,734,720
Influent TSS, mg/L	56	27,000
TSS Loading, lb/day	1,261	360,288
Influent NH ₄ -N, mg/L	404	No analysis
NH ₄ -N Loading, lb/day	9,097	-
Influent TKN, mg/L	404	724
TKN Loading, lb/day	9,097	9,661
Final Effluent Quality	Similar to Groundwater	Similar to Groundwater

^a Updated Process Design for Wastewater Treatment (Gerhardt 2012).

^b Process Design for Biomass Conversion (Davis et al. 2013).

Note: COD = chemical oxygen demand; TKN = total Kjeldahl nitrogen; TS = Total solids; TSS = total suspended solids.

COD, Nitrogen, Temperature, and TSS

As shown in Table 3, Davis et al. (2013) report a higher wastewater concentration of most constituents of concern, but a lower influent flow rate than Gerhardt (2012). Davis et al. (2013) also state higher overall wastewater mass loadings. Gerhardt (2012) considered total COD, NH₄-N, and temperature to be key design parameters, and used them in the cost sensitivity analysis. Because no NH₄-N analysis is available by Davis et al. (2013), TKN values can be used as a good approximation for comparison.

Total COD

Gerhardt (2012) uses a base case design value of 1,500,000 lb/day as the loading to the anaerobic reactors, the first step in the WWT process. Based on this loading, 108 million gallons (MG) of anaerobic reactor volume is provided, with a design goal of 80% total COD removal. The upper bound for the sensitivity analysis is a total COD loading of 1,968,000 lb/day with a recommended anaerobic reactor volume of 140 MG. Concurrently, this higher COD loading results in larger recommended volumes for the aerobic treatment step, which follows the anaerobic process, and also results in increased quantities of waste biological sludge for disposal. Since Davis et al. (2013) calculate a total COD loading for the wastewater of 1,601,280 lb/day, it can be concluded that the resulting wastewater would be treatable relative to total COD using

Gerhardt's treatment process with the appropriate adjustments to anaerobic and aerobic reactor volumes. Gerhardt (2012) estimated a \$6 million increase in installed capital cost in order to handle the 1,968,000 lb/day load.

Nitrogen

In this study, NH₄-N loadings are approximated using TKN loadings. Gerhardt (2012) uses a base case loading of 9,100 lb/day. The highest loading considered is 34,900 lb/day. The impact of the variable NH₄-N loadings has significance in terms of whether or not enough nitrogen is present for biomass growth as the high COD loadings are metabolized, and if nitrification will be required in the aerobic treatment reactors.

Davis et al. (2013) calculated the TKN loading for the wastewater as 9,661 lb/day, less than a 10% increase over the Gerhardt (2012) base case. It is not anticipated that the increased TKN loading would present any treatment problems, or increase installed capital cost significantly.

Temperature and Total Suspended Solids

Wastewater temperature affects biological treatment reaction rates and process efficiencies. Gerhardt (2012) assumes base case influent wastewater temperature to the anaerobic reactor to be 50°C in winter and 30°C in summer, and assumes influent temperature to the aerobic reactor to be 22°C in winter and 35°C in summer. The sensitivity analysis considers an anaerobic reactor influent temperature range that increases to 60°C in winter, and an aerobic reactor influent that increases to 35°C in winter. None of these step changes has a significant impact on process design or installed capital cost. Because the projected influent wastewater temperature in Davis et al.(2013) falls in the same general range as Gerhardt (2012), it is not anticipated that wastewater temperature will affect the design.

Low-rate anaerobic reactor design would be most affected by solids and COD loadings. As can be seen in Table 3, TSS is the one measured parameter where there is a huge difference in loadings between the WWT design wastewater (Gerhardt 2012) and the biorefinery design wastewater (Davis et al. 2013). The influent COD and TS loadings differ by a factor of approximately two between the two types of WWT, whereas the TSS loadings are approximately 300 times higher in the biorefinery design wastewater. This large difference in TSS loadings could have an effect on the sizing of the anaerobic reactors and will definitely have an effect on the quantity of sludge wastage from the anaerobic reactors.

It was initially unclear as to what caused the large increase in influent TSS concentrations, so the sample characterizations and process flow diagrams of all four-design reports (Humbird et al. 2011; Steinwinder et al. 2011; Gerhardt 2012; Davis et al. 2013) were compared in more detail. In the initial WWT design, the wastewater sample TSS concentration measured 14,000–21,000 mg/L. Solids removal, provided by centrifugation upstream of the WWT, resulted in an estimated TSS concentration of 1,500 mg/L. This value was used as the

influent design value for the anaerobic treatment step of the WWT process (Steinwinder et al. 2011).

The critical pretreatment step of removing TSS from the wastewater influent was not included in the biorefinery process design. Yet, the WWT process depicted in the biorefinery design is basically identical to the WWT system proposed in Steinwinder et al. (2011) and Gerhardt (2012).

With respect to sludge production, Gerhardt (2012) estimates that 51 dry tons/day of a 20% solids centrifuge cake will be generated and sent to the biomass burner. It should be noted that neither Gerhardt (2012) nor Davis et al. (2013) consider the possibility of marketing the 20% solids centrifuge cake as a soil conditioner/fertilizer product, as opposed to sending the centrifuge cake to a biomass burner. Because the RDB facility will be located in an agricultural area, it is not clear why marketing the cake as a disposal option was not considered. It is beyond the scope of this report to develop relative cost estimates for land disposal of the biosolids versus the boiler/burner option, but this should be considered in future design reports.

4.6.3 Cost

The WWTP design results were incorporated into the biorefinery design (Davis et al. 2013). The cost estimate for the biorefinery WWT facility was based on the assumption that the WWT system described by Gerhardt (2012) could be used to treat the wastewater generated at this new RDB facility. The biorefinery cost for the RDB facility was based on the estimate of a cellulosic ethanol production process (Humbird et al. 2011). The cost estimate was adjusted for the differences in estimated wastewater flow rates and wastewater strength between the ethanol and the RDB processes, but the basic treatment process scheme, with one exception, remains the same. The one difference is that, in the proposed RDB facility, the brine from the reverse osmosis system would not be sent to the biomass burner system, but would be disposed of separately in an unspecified manner. The estimated installed capital cost (in 2011 dollars) for the WWT system, not including the biomass burner system, was \$65 million. The installed capital cost will be \$76 million if a biomass burner system, comprised of a combustor, boiler, and turbo-generator, is included (Gerhardt 2012).

As mentioned in Section 4.6.2, the centrifuge in wastewater influent pretreatment is also missing from the biorefinery design. Centrifugation is used to remove solids from the wastewater stream to reduce influent TSS to the anaerobic digester from 14,000–21,000 mg/L to the design value of about 1,500 mg/L. If we assume that two centrifuges might be needed for TSS removal in the pretreatment process, approximately \$1.1 million (\$557,000/centrifuge) would be added (Gerhardt 2012) to the WWT process capital costs discussed in Davis et al. (2013). The design of the biomass burner is not significantly affected by this change, as the burner will ultimately receive the same amount of solids. Therefore, the estimated total cost for the WWT, including the burner system and centrifugation units, would be \$77.1 million, up \$12.1 million from the estimate in Davis et al. (2013).

4.7 UNCERTAINTIES, GENERAL COMMENTS, AND FUTURE WORK

In summary, it appears that the wastewater produced by the RDB process described in Davis et al. (2013) can be successfully treated by the WWT system specified in Gerhardt (2012), provided that upstream TSS removal is added and a burner system is installed. However, in order to properly design any WWT system, it is imperative to have good data on the influent wastewater characteristics. The treatment system design described in Gerhardt (2012) is based on one sample each from two different waste streams collected on different days. The biorefinery design (Davis et al. 2013) uses influent wastewater characteristics that come from one sample of a prototype system. It is unclear as to how well these samples represent the day-to-day variation that could occur in wastewater characteristics. This variation adds a significant amount of uncertainty to the design, even taking into account the sensitivity analysis. In addition, the wastewater data does not include parameters such as carbonaceous biochemical oxygen demand (CBOD), total volatile solids, volatile suspended solids, and NH₄-N, all factors a design engineer would typically be interested in knowing. Due to the lack of a robust influent wastewater data set, there is considerable uncertainty as to the exact sizing of the various individual unit processes in the overall design, and thus the overall capital and operating costs of the system could differ from those stated in the process designs.

Future experimental work should make an effort to collect multiple wastewater samples from the process and analyze the samples for the traditional parameters listed above. A complete sampling point analysis—samples analyzed prior to and after pretreatment for multiple batches of reactor runs—will provide a representative set of influent characteristics so that the entire WWT process can be understood and firm costs determined. Finally, land application of any biosolids produced by the WWT process should be considered as an economical alternative to solids combustion.

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APPENDIX: INFORMATION ON OTHER POSSIBLE WASTEWATER TREATMENT TECHNOLOGIES

An attempt was made to determine if other treatment technologies for processing the wastewater generated by the renewable diesel blendstock (RDB) process were commercially available, and to collect any available cost data on such processes. As the RDB process is an innovative technology, it was not expected that any commercially available systems would be designed specifically to treat the type of wastewater produced by this process. A review of trade publications and equipment manufacturer websites led to a few possible treatment alternatives, but it was clear that very few operating facilities exist that treat wastewater flows on the scale of the proposed RDB facility. These facilities are privately owned and it is difficult to get detailed information from them on process design or costs.

Two equipment distributors were identified who provide wastewater treatment (WWT) systems for large biofuel projects. However, neither of them has actual operating WWT systems installed in the United States. One, A3 Water Solutions GmbH, has facilities operating in Europe. The other, Team Gemini LLC, has pilot scale facilities in the United States and is building a large facility in Canada.

The A3 Water Solutions GmbH system is advertised as a multiphase separation system, which takes the wastewater stream from a biofuels process and sends it to a solid/liquid separation system consisting of a screw press and/or decanter centrifuge, followed by ultrafiltration, and then reverse osmosis treatment. The treated liquid can be recycled as process water and the solid residues from the screw press, centrifuge, and ultrafiltration system are distributed as a soil conditioner/fertilizer product. The brine is disposed of separately.

The Team Gemini LLC system takes the wastewater stream from the biofuels process and sends it to a solid/liquid separation system consisting of a vibrating screen and/or decanter centrifuge, followed by ultrafiltration, and then reverse osmosis treatment. The treated liquid can be recycled as process water and the solid residues are distributed as a soil conditioner/fertilizer product. The brine is sold as a high strength commercial fertilizer solution.

DuPont Corporation is building a large biofuels facility in Nevada, Iowa, which use a proprietary process for converting agricultural waste to ethanol. The wastewater stream is sent to a filtration system, and the filtrate is then sent to an evaporator. The evaporator residue is combined with the solids captured by the filtration system and sent to a biomass boiler/dryer system, which produces a solid fuel product. The water from the evaporator is recycled as process water.

At this time, it has not been possible to obtain cost data for any of the above treatment systems.

Both Gerhardt (2012) and Davis et al. (2013) assume that the biofuels facilities will be located in rural areas without access to municipal water or wastewater facilities. This assumption is one of the driving factors in the design of the WWT process train. It is also assumed that an

RDB facility could be located in Iowa, and the possibility of locating an RDB facility in the service area of one of the larger metropolitan areas in Iowa was investigated. The City of Des Moines, Iowa, operates a regional WWT facility that encompasses Des Moines and a number of surrounding communities. The design flow of the facility is approximately 97 million gallons per day (MGD) and it accepts industrial discharges to its sewer system, as long as they meet pretreatment program requirements. The industry pays a user charge based on CBOD, TSS, and TKN loading to the system. The 2015 rates are \$0.11/lb CBOD, \$0.16/lb TSS, and \$0.61/lb TKN. Gerhardt (2012) estimates that the effluent from the anaerobic reactors will have a CBOD of 2,600 mg/L, a TSS of 800 mg/L, and a TKN of 404 mg/L. Assuming a similar anaerobic reactor effluent quality from Davis et al. (2013) and a wastewater flow of 1.6 MGD as specified in the report, the calculated user charge to discharge the anaerobic reactor effluent directly to the Des Moines sewer system would be \$8,812/day. In addition, municipal water would have to be purchased for process water, as no wastewater would be recycled under this scenario. The cost of purchasing 1.6 MGD of water from Des Moines is \$3,168/day. This works out to a total annual cost for user fees plus water fees of \$3.36 million. Although this is a large operating cost, this option would allow elimination of the aeration reactors, membrane filters, reverse osmosis units, and gravity belt thickeners from the design of the treatment facility. Also, if the waste sludge from the anaerobic reactors could be centrifuged and then used as a soil conditioner/fertilizer product, the burner/boiler system could be eliminated from the design. It is beyond the scope of this report to determine the cost implications of such a major process change, but this option should be investigated if it was determined that one of the RDB facilities could be located near Des Moines.



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